

The University of Chicago

SATURATED FILMS
AND A COMPARISON OF THE FILM
BALANCE AND THE RING METHOD
FOR SURFACE TENSION

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By
HENRIETTA NOAH DA COSTA

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1933

The University of Chicago

SATURATED FILMS
AND A COMPARISON OF THE FILM
BALANCE AND THE RING METHOD
FOR SURFACE TENSION

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By
HENRIETTA NOAH DA COSTA

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1933



Digitized by the Internet Archive
in 2026



TABLE OF CONTENTS

I. A study of saturated films by the ring method.	1-14
II. A comparison of the ring method and film balance method of determining surface tension.	15-18
III. A study of saturated films and mixed films with the film balance.	
A. Saturated films	19-22
B. Mixed films.	23-29



I. A Study of Saturated Films by the Ring Method

1. Introduction

According to the phase rule two phases may be present in a system which consists of one component provided there is one degree of freedom. If one of the phases is a vapor, then the vapor pressure is a function of the temperature alone, provided equilibrium is attained, which is one of the conditions used in the development of the rule. If some solid stearic acid, or a drop of oleic acid, is put on the clean surface of some water, then it is found that the equilibrium pressure, against a barrier, produced by the film of material which spreads from the solid or the liquid, is dependent on temperature alone.

That this is true has been known for a long time, and is shown by the recent work of Rideal and Cary (1). They obtained values for the surface tension (γ') for films in equilibrium with solid myristic acid and other solid organic substances. The pressure of the film (F) in dynes per centimeter is considered to be equal to the surface tension of pure water (γ) minus the surface tension of water covered with the film (γ'), or

$$\gamma - \gamma' = F$$

Now if it is assumed that the equation of Clapeyron

$$\frac{\partial F}{\partial T} = - \frac{\lambda}{TA}$$

(1) Cary and Rideal, Proc. Roy. Soc. (London) A. 109, 318 (1925)
Also Lyons and Rideal, *ibid.*, 124, 322, 331 (1929)
and Schofield and Rideal, *ibid.*, 110, 167 (1926)

is valid for this case, then the latent heat of spreading may be calculated.

Rideal and Cary used the ring method to determine the surface tension of the film, and calculated their results by the use of the equation

$$\gamma = \frac{Mg}{4\pi R}$$

which has been shown by Harkins, Young, and Cheng (2), to be incorrect. The correct equation is

$$\gamma = \frac{Mg}{4\pi R} \phi$$

Since the value of ϕ varies rapidly with the surface tension, the values of the film pressure and especially of the heat of spreading calculated without the inclusion of this function may be very far from correct.

2. Apparatus

The apparatus used is a two liter pyrex flask with an enclosed dish which contains the liquid whose surface tension is to be measured. There are four openings in the flask. The first (A of Fig. 1) extends vertically upwards and is used to admit the ring attached by an aluminum chain to one end of the beam of a chainomatic balance. Another opening (B) communicates from beneath with an inner dish and through it new liquid is introduced so as to overflow from the dish (C) and form a clean surface. The third opening (D) is used to withdraw the liquid which accumulates in the bottom of the flask.

(2) Harkins, Young, and Cheng, Science, 64, 333 (1926)

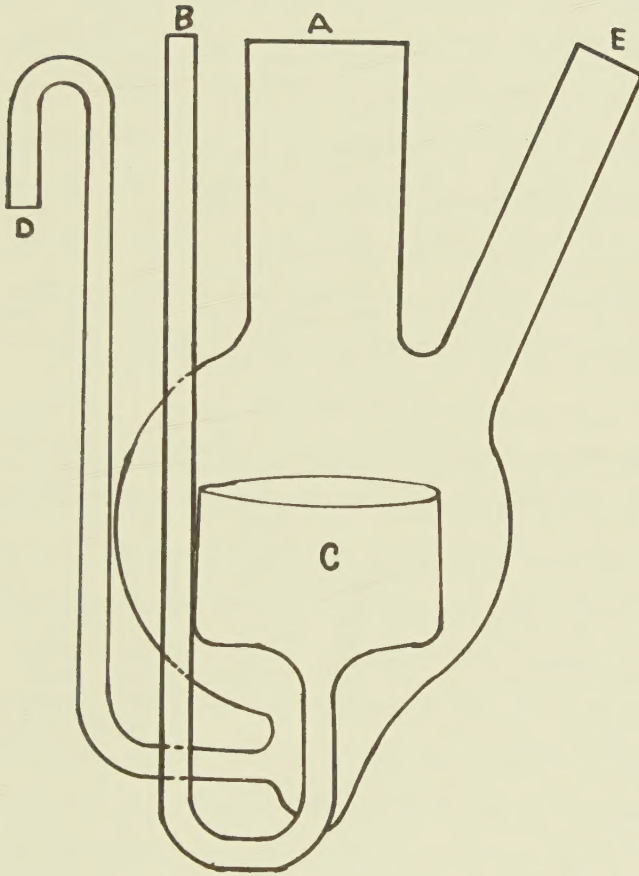


FIG. 1

The fourth opening (E) is at an angle and serves for the introduction of a glass stirring rod previously dipped in the substance to be spread on the surface. The flask is used in a constant temperature water bath in which the maximum deviation of the temperature at the highest and lowest temperatures was 0.05 degrees C. At temperatures nearer to that of the surroundings the regulation was better, at 25°C. and 30°C. being $\pm 0.01^{\circ}\text{C}$. It was necessary to stop stirring while taking a reading because jarring the apparatus disturbed the surface adjacent to the ring. The pull of the ring is determined by a chainomatic balance on a support which permits it to be raised or lowered with a minimum of friction (3).

3. Procedure

The myristic acid and cetyl alcohol samples were obtained from the Eastman Kodak Company and were purified by intimately mixing with three liters of hot conductivity water three times and recovering that which was still insoluble. This was to remove any possible water soluble substances. The palmitic acid was a Kahlbaum product and was purified by dissolving in hot 95% ethyl alcohol, filtering and pouring the solution into a large excess of conductivity water. This was done three times.

The experimental procedure consisted of filling the inner dish with either conductivity water or 0.01 N. hydrochloric acid. The flask was immersed in the constant

(3) Harkins and Jordan, J. Am. Chem. Soc., 52, 1751 (1930)

temperature bath and left to assume the temperature of the bath, the length of time required depending on the difference between the temperature and that of the surroundings. Then a little more liquid was added from beneath the surface, so as to obtain a fresh surface, and immediately it was touched with a stirring rod dipped in our molten organic substance. It spread completely over the surface from the point of contact and some solid remained on the surface. Some of the substance dissolved to form a surface film in equilibrium with the solid. Then the ring was lowered to the surface until it just touched and was left there until equilibrium in the film had been attained. The time for this to occur differed for various substances and conditions and was easily found by a series of measurements with a given set of conditions. As a whole the time to attain equilibrium decreased with rise of temperature with any given system. When equilibrium was attained the ring was gradually raised and the maximum weight necessary to balance the pull of the liquid on the ring was observed. The surface tension was calculated by the use of the equation of Harkins and Jordan (3).

$$\gamma = \frac{Mg}{4 \pi R} \phi$$

γ = Surface tension.

R = Radius of ring.

ϕ = Correction factor (Depends on $\frac{R}{r}$ and $\frac{R^3}{V}$)

TABLE I

VARIATION OF SURFACE TENSION AND
FILM PRESSURE WITH TEMPERATURE

T°C.	γ_{H_2O}	$\gamma_{P.A.}$	$F_{P.A.}$	$\gamma_{C.A.}$	$F_{C.A.}$	$\gamma'_{M.A.}$	$F'_{M.A.}$	$\gamma_{M.A.}$	$F_{M.A.}$
0	75.6	54.5	21.1	46.5	29.1	67.2	8.4	61.7	13.8
5	74.9								
10	74.2	52.0	22.2	44.6	29.6	61.2	13.0	57.6	16.6
15	73.5					57.2	16.3		
20	72.8	49.0	23.8	41.4	31.4	54.6	18.2	53.8	19.0
25	72.0					50.6	21.4		
30	71.2	45.7	25.5	36.2	35.0	47.1	24.1	49.5	21.7
35	70.4			31.6	38.8	44.1	26.3		
40	69.6	41.6	28.0	31.7	37.9	41.0	28.6	45.1	24.5
45	68.7					37.8	30.9		
50	67.9	37.0	30.9	32.5	35.4	34.3	33.6	39.4	28.5
55	67.1					31.2	35.9	37.2	29.9
60	66.2	37.0	29.2	31.2	35.0	29.7	36.5	34.2	32.0
65	65.3	36.8	28.5			28.6	36.7	34.3	31.0
70	64.4					27.3	37.1	34.2	30.2

T°C. = temperature in degrees centigrade.

γ_{H_2O} = surface tension of water.

$\gamma_{P.A.}$ = surface tension of 0.01 N. HCl with palmitic acid.

$\gamma_{C.A.}$ = surface tension of 0.01 N. HCl with cetyl alcohol.

$F_{P.A.} = \gamma_{H_2O} - \gamma_{P.A.}$

$F_{C.A.} = \gamma_{H_2O} - \gamma_{C.A.}$

$\gamma_{M.A.}$ = surface tension of water with myristic acid.

$\gamma'_{M.A.}$ = surface tension of 0.01 N. HCl with myristic acid.

$F_{M.A.} = \gamma_{H_2O} - \gamma_{M.A.}$

$F'_{M.A.} = \gamma_{H_2O} - \gamma'_{M.A.}$

Each γ value represents an average of from three to five separate films.

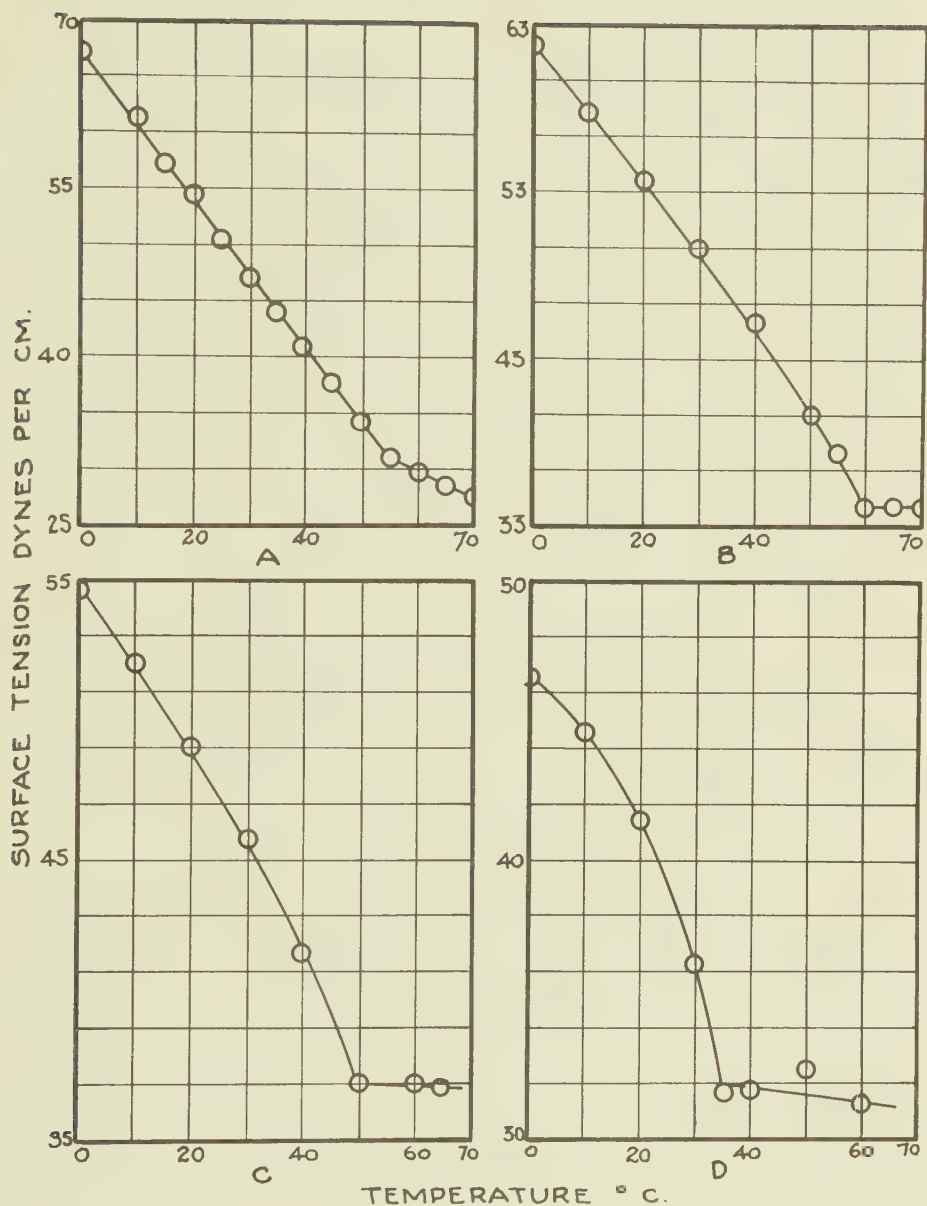


FIG. 2.

(A) MYRISTIC ACID ON WATER; (B) MYRISTIC ACID ON 0.01 N HCl; (C) PALMITIC ACID ON 0.01 N HCl; (D) CETYL ALCOHOL ON 0.01 N HCl.

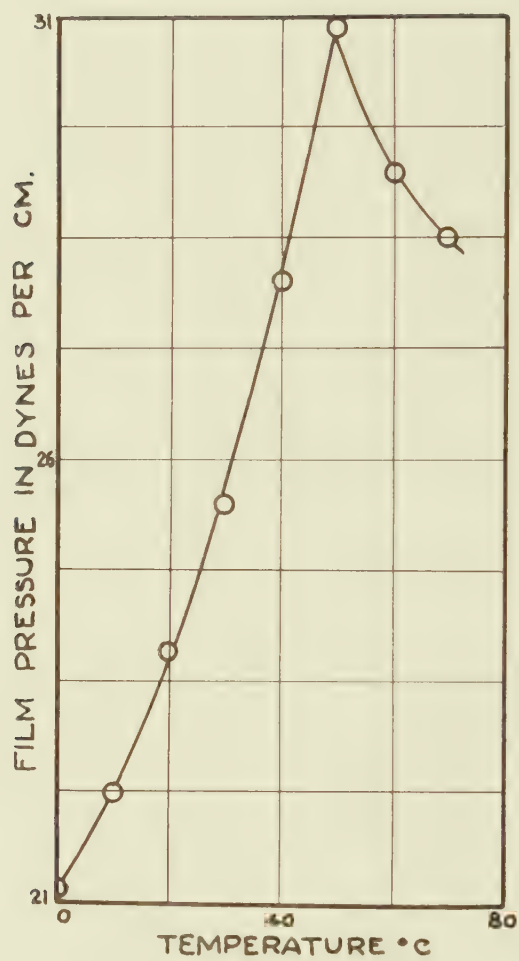


FIG. 3

PALMITIC ACID ON 0.01 N. HCl.

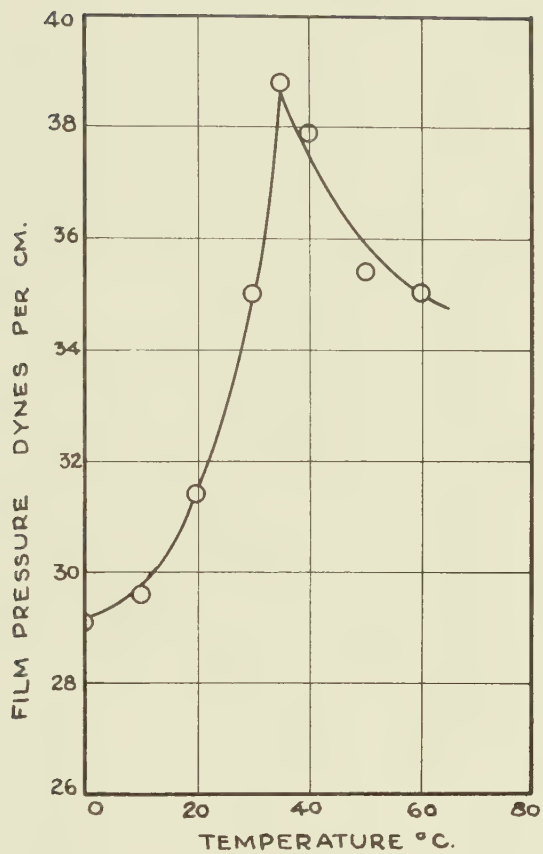


FIG. 4.

CETYL ALCOHOL ON 0.01N.HCl.

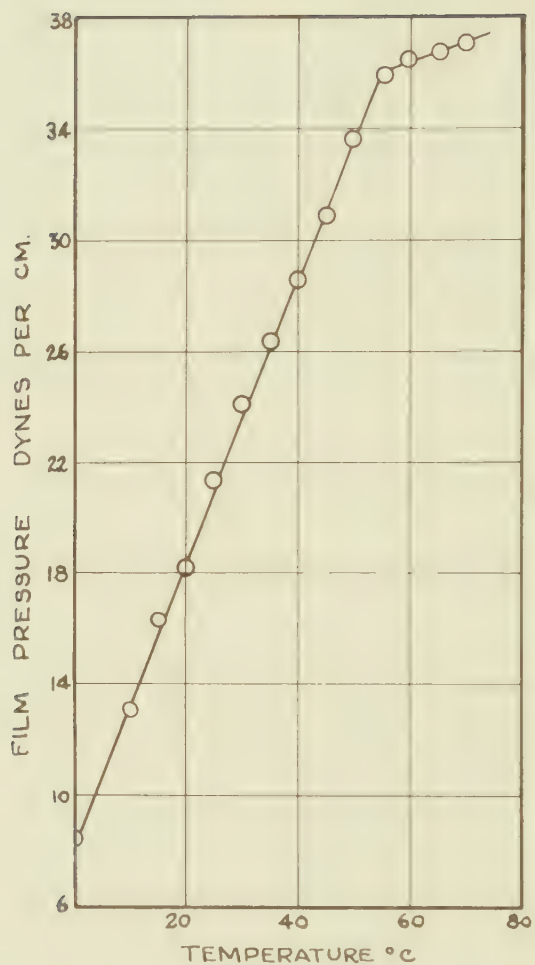


FIG. 5
MYRISTIC ACID ON WATER

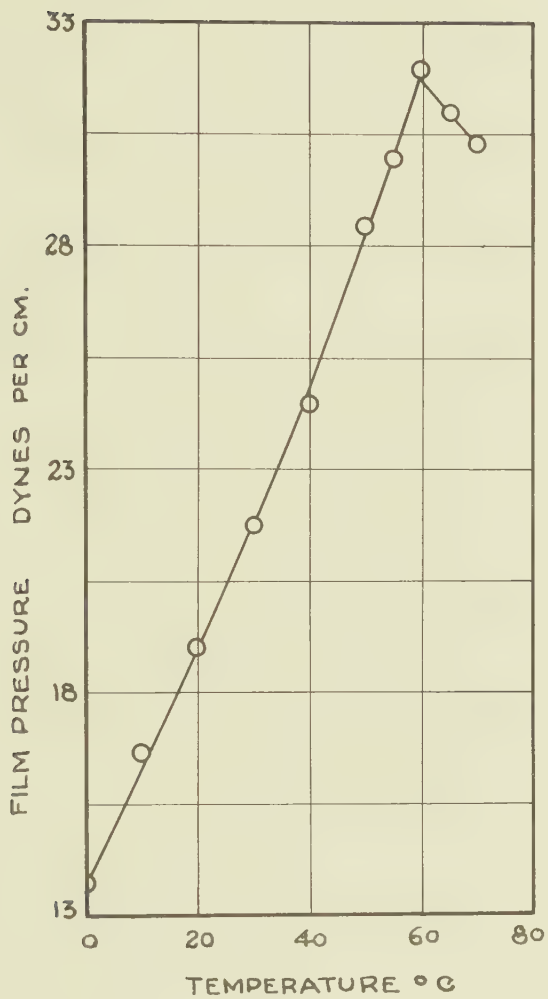


FIG. 6.
MYRISTIC ACID ON 0.01 N. HCl.

4. Data and Calculations

The data were plotted with the surface tension as ordinates and temperature in degrees centigrade as abscissae. All substances on 0.01 N. hydrochloric acid give a surface tension which decreases with temperature until a transition temperature is reached and then the surface tension remains constant. In the case of the two acids (myristic and palmitic) the slope is fairly constant. With myristic acid on water the slope is constant and, at a transition temperature, the slope decreases but does not become zero. If, however, the film pressure, or decrease in surface tension, is plotted as ordinates against temperatures in degrees centigrade as abscissae, a straight line is obtained until the transition temperature, when the slope becomes almost zero. In all the other cases the film pressure increases to a maximum and decreases again, in each case having the same slope after the transition (Table II).

By the use of this latter curve the latent heat of spreading of the organic substance on the given liquid is calculated from the modified two-dimensional Clapeyron equation. If the slope is constant for a system then the latent heat of spreading on the surface increases directly as the temperature, which is the case for myristic acid spread on water. After the transition temperature the latent heat of spreading for this system is almost zero. For the other systems the latent heat changes slightly with the temperature until near the transition temperature, where the change is great and the value

of the latent heat changes sign. In all cases the transition temperature is near the melting point of the organic solid, so the transition may be caused by a change in crystal form and a corresponding change in type of film.

From Table II the latent heat of spreading of these substances as a solid or a liquid film is obtained at the transition temperature. On 0.01 N. hydrochloric acid the latent heat of spreading per mole for all three substances as liquid or solid is of the same order of magnitude. For myristic acid on water the mechanism of spreading is different, since the latent heat is not only of a different order of magnitude, but also of reverse sign. For the liquid film on dilute acid Rideal (1) gives the value of 1600 calories per mole for the latent heat of spreading. This agrees with our values for liquid films on dilute acids at the transition temperature. With solid films on dilute acid Rideal obtains 5620 for palmitic acid at 18°C. and 8070 at 30°C. for myristic acid, or much higher values for λ than in our work. The difference in the case of myristic acid is partially explained by the fact that a larger cross-section is assumed by Rideal ($30 \text{ \AA}^2$ + depending on the temperature). The slopes of both parts of the curve of myristic acid are the same, but this is not true for palmitic acid. These data give the order of magnitude of the heat of spreading of a solid or liquid organic acid or alcohol on dilute acids or water.

TABLE II
LATENT HEATS OF SPREADING

Substance	Slope before transition	Slope after transition	Transition temperature	λ in cal./mole	
				Solid	Liquid
Palmitic acid on 0.01 N. HCl	0.269	-0.175	323	-2500	1700
Cetyl alcohol on 0.01 N. HCl	0.370	-0.170	308	-3400	1600
Myristic acid on 0.01 N. HCl	0.563	-0.175	333	-5600	1700
Myristic acid on H ₂ O	1.01	0.080	328	-9900	- 800

TABLE III
COMPARISON OF DATA WITH THOSE OF RIDEAL

	Myristic Acid			Palmitic Acid		
	Slope before transition	Slope after transition	T	Slope before transition	Slope after transition	T
(Rideal)	0.568	-0.163	336	0.554	-0.163	327
(My work)	0.563	-0.175	333	0.269	-0.175	323

II. A comparison of the ring method and film balance method of determining surface tension

1. Introduction

This work was undertaken in order to obtain a comparison of the surface tension of water when covered with a film as determined by the ring method or by the use of a film balance of the type devised by Adam.

2. Experimental

The special film balance used is one developed in this laboratory and is described in detail by Freud (4). The clean, well-paraffined tray is filled with conductivity water and the film balance placed on the surface and the zero reading taken after the surfaces on both sides of the balance had been swept very thoroughly several times. Then a small amount of a benzene solution of a spreading substance is placed on the left side of the balance and the float brought back to the initial position. Since the balance is calibrated, this gives the film pressure. On this film is placed the ring attached to the chainomatic balance and a mechanism which serves to adjust the height of the balance. The value of the surface tension is determined by the ring method. Since the film balance gives the difference in surface tension between two sides of the balance, it is necessary that the far side be clean and that no leaks occur. This was tested by a determination of the surface tension of the supposedly clean water surface by

(4) B. B. Freud, Ph.D. thesis, University of Chicago, 1927.

the ring method. Immediately after sweeping the surface tension was found to be within 0.1 dyne/cm. of that of water. If left unswept for a longer period, the surface tension fell to only 0.5 dyne/cm. lower than that of water and, after attaining this value, changed only negligibly. This seems to indicate that the small amount of contamination was caused by impurities in the air and not by a leaking of the film past the gold foil at the ends of the float.

3. Data and conclusions

When the calculated values of lowering of surface tension as determined by means of the two methods are compared, certain discrepancies are evident. For low film pressures the film pressure is always the lower, but for higher pressures, the deviation is in either direction. A table of typical results follows this discussion.

It is possible that the film balance gives only the average pressure of a film, which is monomolecular in spots but is not uniform. For low pressures the surface tension is not lowered so much near the edge as at the center, where the ring is placed. At higher pressures the same non-uniformity persists, but the ring may be in places thicker or thinner than average, which accounts for either value being larger. If this explanation is correct, equilibrium is not attained between different parts of the film. While this might not be the explanation, the fact remains that the two methods at moderate and high pressures preserve fair agreement, while at low pressures the discrepancy is large. It is also possible

that the ring method is only accurate with uniform surfaces, so the results should not be expected to be the same in both cases.

TABLE IV
COMPARISON OF SURFACE TENSION DETERMINED
BY FILM BALANCE AND RING METHOD

F	$-\Delta\gamma$	Differ- ence F - ($-\Delta\gamma$)	F	$-\Delta\gamma$	Differ- ence F - ($-\Delta\gamma$)	F	$-\Delta\gamma$	Differ- ence F - ($-\Delta\gamma$)
0.4	8.4	-8.0	10.8	12.0	-1.2	20.1	18.9	1.2
0.7	8.4	-7.7	10.8	11.5	-0.7	20.2	19.3	0.9
1.7	8.8	-7.1	11.1	11.7	-0.6	20.2	18.6	1.6
1.7	9.0	-7.3	11.4	9.2	2.2	20.5	18.8	1.7
2.2	7.8	-5.6	11.8	9.2	2.6	20.8	19.1	1.7
4.9	6.1	-1.2	17.7	18.9	-1.2	21.0	19.3	1.7
5.0	6.6	-1.6	17.8	19.6	-1.8	21.1	22.1	-1.0
5.2	7.2	-2.0	18.0	19.1	-1.1	21.1	21.7	-0.6
8.3	7.9	0.4	18.1	19.9	-1.8	21.2	22.1	-0.9
8.5	7.4	1.1	18.5	19.7	-1.2	21.5	19.6	1.9
9.6	11.0	-1.4	19.2	18.0	1.2	21.5	22.6	-1.1
9.7	11.0	-1.3	19.3	17.9	1.4	23.0	20.1	2.9
9.7	10.9	-1.2	19.4	18.4	1.0	25.2	23.0	2.2
10.1	10.2	-0.1	19.6	18.6	1.0	25.3	23.3	2.0
10.4	11.3	-0.9	19.8	18.5	1.3	25.6	23.4	2.2
10.5	11.6	-1.1	19.9	18.5	1.4	25.7	23.4	2.3
10.7	12.0	-1.3	20.0	18.7	1.3	25.8	23.3	2.5
10.8	11.8	-1.0				25.9	23.8	2.1

F = Film pressure in dynes.

$-\Delta\gamma$ = Decrease in surface tension by ring method.

Each value represents one film.

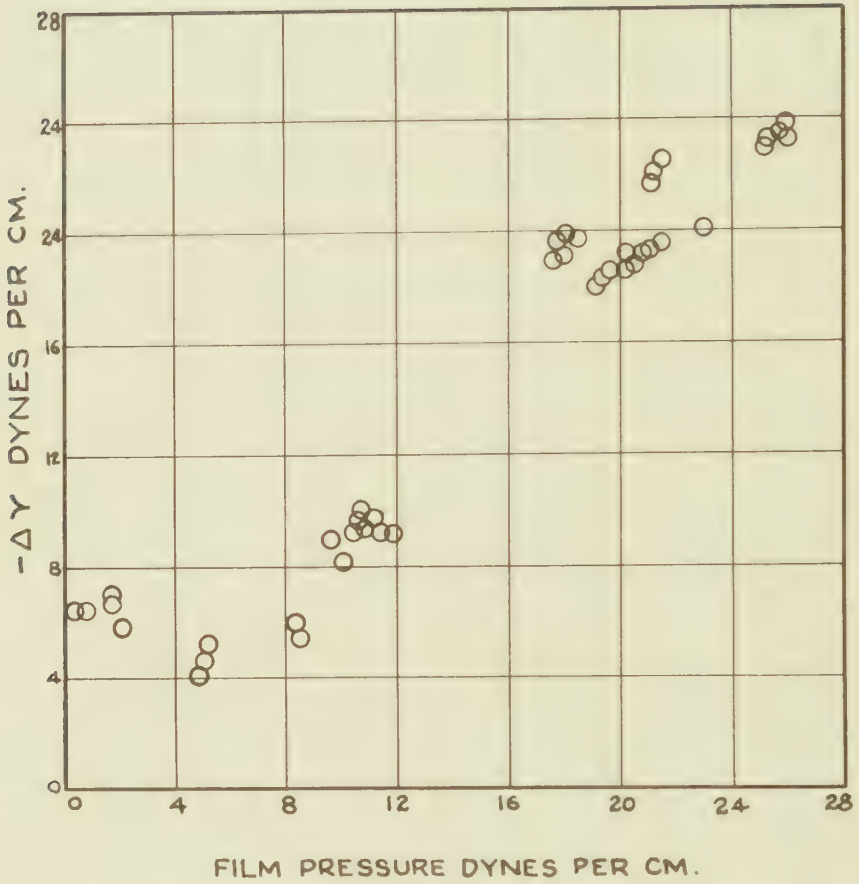


FIG. 7

COMPARISON OF FILM BALANCE AND RING METHOD OF
DETERMINING SURFACE TENSION. FILMS OF PALMITIC
ACID.

III. A study of saturated films and mixed films with the film balance

A. Saturated films

1. Introduction

A comparison of film pressures of saturated films as obtained by the film balance with those with the ring method was undertaken in order to determine to what extent and under what conditions the two methods give the same results.

2. Experimental

In order that values given for pressures with the film balance be reliable, the initial and final positions of the float must be the same. For work over a long period of time this is essential. The lateral position is located by focusing the cross-hairs of a telescope on a scale which is reflected in the mirror attached to the float. The float is returned to its original position, in which there is a minimum of force acting on the float. If the vertical height of the float is changed, then at the zero as indicated on the scale the float will not be in the original position with respect to a horizontal displacement. Since the float rests on the water surface, it is necessary to keep the latter at the same vertical height. The ideal position for the surface is determined and indicated by the lower end of a fine wire. If out of adjustment, the surface is raised or lowered by addition or removal of water from a side tube.

The only convenient type of constant temperature bath for this work is an air thermostat, in which the temperature

is equalized by a fan. This causes ripples on the surface of the water and makes the film unsteady. At any speed capable of satisfactorily mixing the air this occurred. With some shielding the effect was greatly decreased, but films which required a long time to attain equilibrium could not be used, as the fan could not run during the entire life of the film.

The equilibrium film pressure of myristic acid on conductivity water was the only material for which a series of measurements was made. The procedure consisted of dipping a stirring rod coated with the substance into a freshly swept water surface. As the pressure increased, the float was gradually returned to the original position. When this had attained a constant value it was considered equilibrium.

3. Data

With myristic acid the film pressure varied linearly with the temperature. A table and graph which compare values obtained with the film balance and ring follow. In Table VI are the values of latent heat of spreading, λ , of myristic acid on water at 30°C. They are calculated from the modified Clapeyron equation used previously. The values are somewhat different, and it seems probable that the values do not represent a measurement of the same thing. When the film spreads on the water in a dish ten centimeters in diameter, well shielded from air currents, as when the ring method is used, equilibrium is readily attained. However, if the surface is large, as in the use of the film balance, true equilibrium may not be attained. The air currents affect it much more,

even when the apparatus is in an enclosed space.

TABLE V
FILM PRESSURES WITH BOTH FILM BALANCE AND AS
DECREASE IN SURFACE TENSION (RING METHOD)

t	F	- $\Delta\gamma$
15	12.3	16.3
20	16.0	18.2
25	19.5	21.4
30	23.8	24.1
35	27.8	26.3

TABLE VI
COMPARISON OF LATENT HEATS OF SPREADING FROM
DATA OF FILM BALANCE AND RING METHOD

	Slope	λ at 303°K.
Ring method	0.525	-4.8×10^3 cal./mole
Film balance	0.725	-6.6×10^3 cal./mole

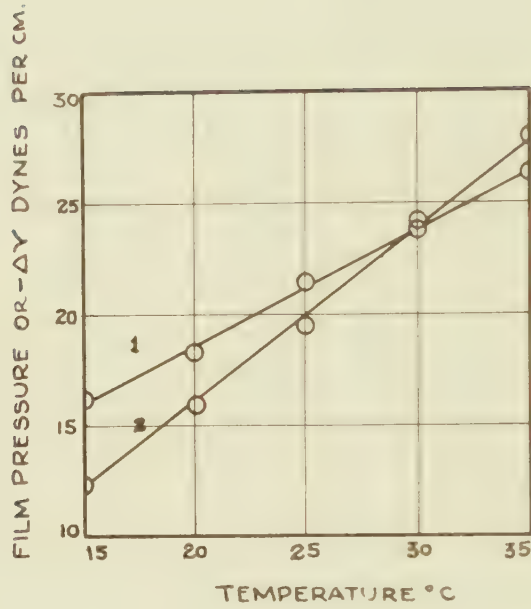


FIG. 8.

SATURATED FILMS OF MYRISTIC ACID
ON WATER WITH (1) RING METHOD
AND (2) FILM BALANCE

B. Mixed films

1. Introduction

Previous work on mixed films has been done by Harkins and Morgan (5). This part of the work is a continuation of that investigation.

2. Experimental procedure

Solutions were made from Kahlbaum's stearic acid and the Eastman Kodak Company's phenanthrene in Mallinckrodt's "reagent quality" benzene. The concentration was such that 0.2 cc. gave a film which covered half the available surface of the entire tray.

The solutions were applied in three ways on the freshly swept water surface: (1) applied in one place so the spreading occurred from one lens of solution; (2) applied a drop at a time at random over the surface, so that the spreading occurred from a number of small lenses; and (3) each small lens was given the maximum space in which to spread so as to avoid any possible overlapping or hindrance to spreading by film already present. The restriction was applied by clamping a barrier at a definite position so that all of the area of the film side of the surface was not available.

3. Data and conclusions

In this work curves similar to those for stearic acid were found, though usually the curve was not so steep. The area per molecule was calculated on the basis of the number

of molecules of stearic acid present, and was found to be larger in general than for stearic acid alone, but not large enough to consider the two areas as additive. However, any correlation of amounts of non-spreading substance present with the extrapolated area was rendered difficult by the great variance in the films under different conditions. If fairly concentrated solutions were used there was not much difference, but if the solutions were dilute, the film which it formed after evaporation of the solvent collapsed before any appreciable pressure was attained. The spreading area was, however, very much greater.

The method of application of the solution influenced the extrapolated area as well as the strength of film. The composition was varied and in the first set of experiments the mole ratio (P/S) of phenanthrene to stearic acid was four. If this solution was applied all in one place, the normal cross-section area for stearic acid was obtained. For solutions applied a drop at a time the area was larger and varied from $27 \text{ \AA}^2$ to $34 \text{ \AA}^2$ according to the amount of restriction on the film while it was being formed. When the film was limited to a restricted area during formation, it did not spread further when the pressure was released (Fig. 10). With a solution of the same constituents but a mole ratio (P/S) of three, similar results were obtained (Fig. 9). However, when the area available for spreading was restricted sufficiently, a normal molecular area was obtained even when the solution was applied a drop at a time. However, these films were much weaker, and

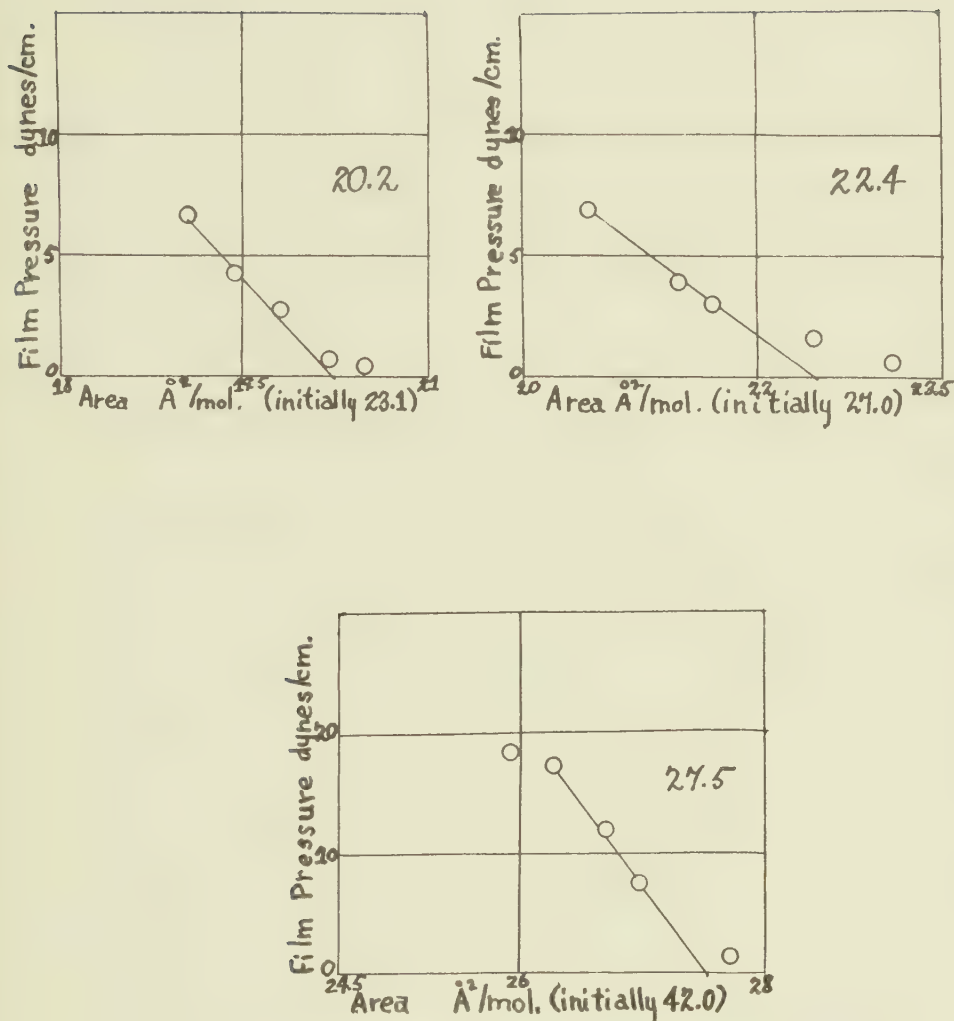


Fig.9. Typical curves of mixed films, mole ratio(P/S) of 3. All applied method(2).

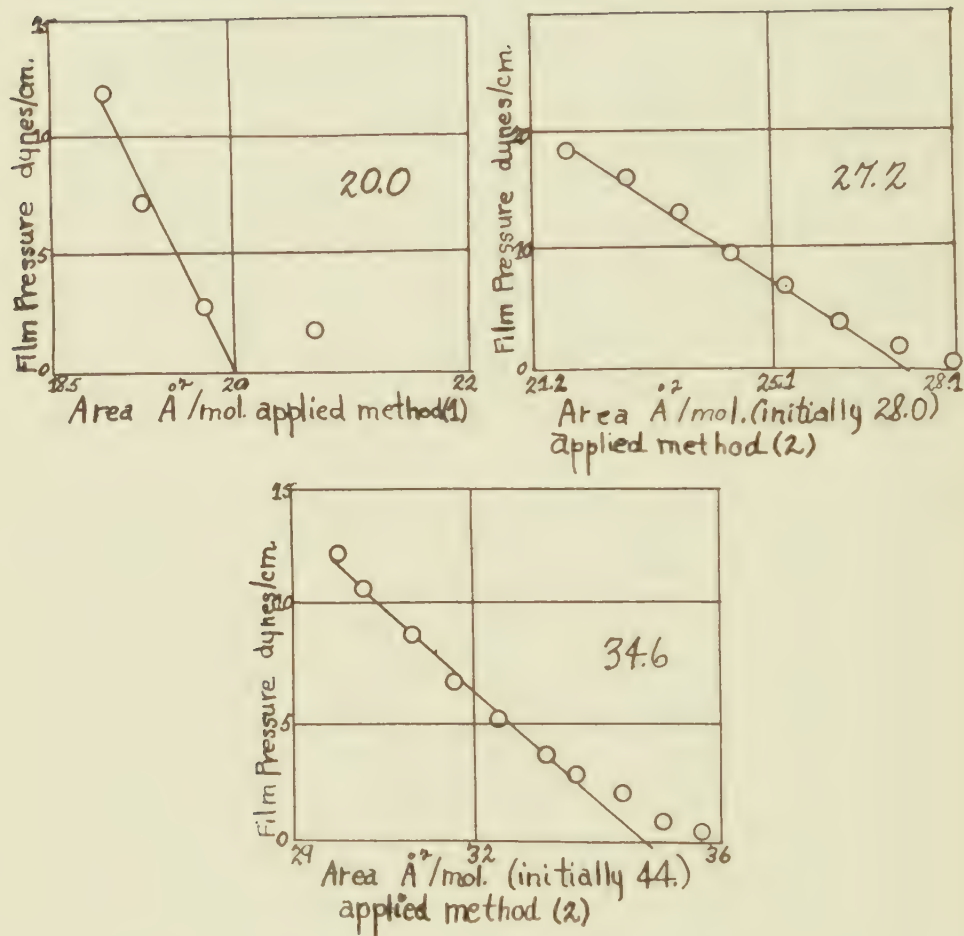


Fig.10. Typical curves of mixed films,
mole ratio (P/S) of 4.

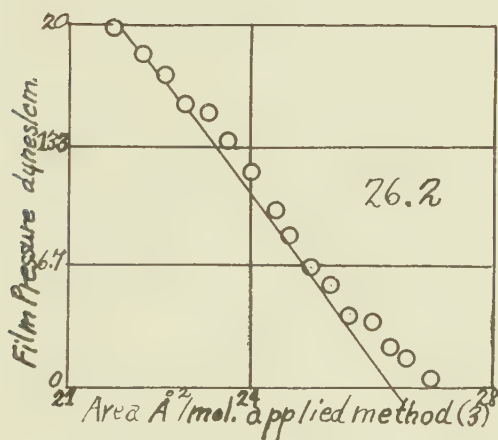
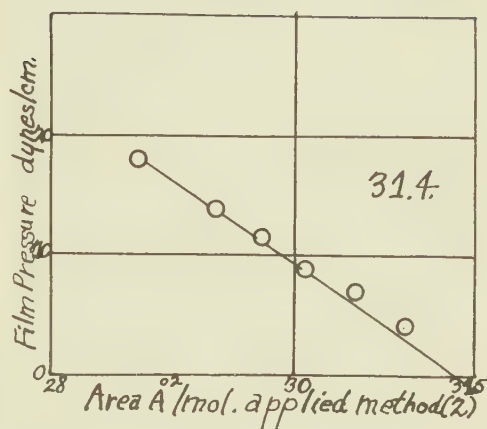
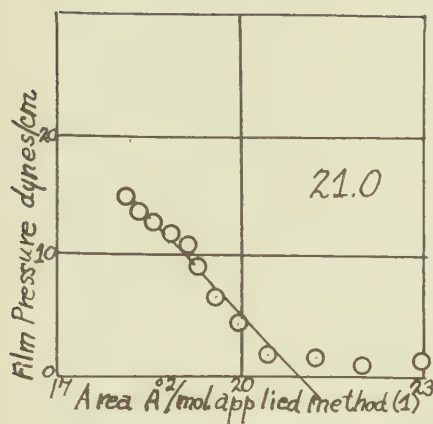


Fig. 11. Typical curves of mixed films, mole ratio (P/S) of 7.77.

TABLE VII
MIXED FILMS

Ratio P/S	Initial Area	Area	Restriction	Application
3.00	23.1 $\text{\AA}^2$	20.2 $\text{\AA}^2$	(a)	(2)
"	27.0	22.4	(b)	(2)
"	42.0	27.5	(c)	(2)
4.00		20.0		(1)
"	28.0	27.2	(b)	(2)
"	44.0	34.6	(c)	(2)
7.77		21.0		(1)
"		31.4		(2)
"		26.2		(3)

(a) Highly restricted during formation

(b) Partially restricted " "

(c) No restrictions " "

Numbers refer to description in experimental part.

most of them collapsed before ten dynes pressure was reached. Even with these substances in mole proportions (P/S) of 7.77 for the solution applied in a stream with an excess of spreading area, the extrapolated area was around $20.7 \text{ \AA}^2$ (Fig. 11). With the second method of application, the area was larger, but in the same range as previous solutions. The third method of application gave more spreading but weaker films. In no case was the area restricted, and the films were stronger than in the previous case when they were restricted.

Evidently if given sufficient room for spreading, the stearic acid spreads and carries the phenanthrene with it. Otherwise, if any barriers prevent spreading, the phenanthrene prevents the stearic acid from spreading further to attain equilibrium after the film has been formed. The film is thus not reversible. The factor of initial conditions is more important than actual concentration of film if the area occupied per molecule is considered. The non-spreading substance fixes the film so that it cannot attain an equilibrium condition which depends on the concentration.

I wish to express my gratitude and appreciation to Professor W. D. Harkins whose advice and coöperation made this work possible.

